

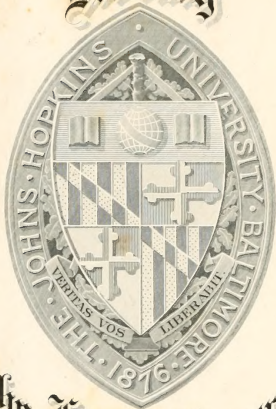
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Johns Hopkins University
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The Double Salides
of
Lead and the Alkalies,
min

A Dissertation

Presented to the Board of University Studies of the
Yale University for the Degree
of Doctor of Philosophy,

by
Chas. H. Seely,

1890

— " —

54-379

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~~~~~



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# Intradirection

There is a very sharp distinction  
was drawn between the Oxygen  
acids and bases. But when this  
sharp distinction no longer  
holds good, for many  
substances act either as acid or  
base, according to the nature  
of the substance with which it  
combines, then Aluminium  
Hydroxide when treated with strong  
acids acts as a base, giving rise  
to Aluminium salts of the acids,  
when treated with ~~strong acids~~ ~~strong~~  
strong bases it acts as an acid,  
giving rise to a class of compounds  
called Aluminates. In fact the  
Oxygen compounds form a





continuous series, in which  
beginning with the strongest bases,  
the basic properties gradually  
diminish while the acid properties  
increase.

Just as the acidic oxides combine  
with the basic oxides to form  
salts, so, according to  
Ure & Bunsen, "strong acids  
combine with basic oxides  
to form compounds analogous  
to the salts."

In the same year, 1826,  
Berzelius called attention to the similarity  
between the oxides, halides, & sulphides,  
& put forward the view that just as  
any two oxides & bases combine to form

---

(1) - Ann. Chim. phys. [2], 34, 142

(2) - Ann. Chim. phys. [2] 34, 331



oxygensalts, so halides combine with each other to form true salts; similarly sulphides combine with each other to form sulpho salts,

In 1840 Dr Kane of Philadelphia in his Compendium recognized the close analogy between the true Sulpho Chloro Bromides & Iodide salts,

But these views of Van Bunsdorff, Baillay and Kane were not generally accepted. The majority of Chemists were satisfied with considering these bodies molecular compounds. They were true chemical compounds. In accordance with this idea they expressed the composition of these bodies in the following manner -



$MgCl_2, KCl$

$U_2F_{10}$

"Professor Reuss" of the  
Siberian Mining University in an  
extended article on the "Nature  
and Structure of the Double Salts"  
has shown that from examination  
of the composition of his large  
class of compounds the following  
law may be deduced; -  
"When a double salt is formed  
between with a halide of an  
alkali metal to form a double  
salt, the number of molecules  
of the ~~stronger~~ alkali salt which  
are added to one molecule of  
the other halide is never greater

---

4 - Amer. Chem. Soc. Vol. 11 p. 291



and is generally less than the number of halogen atoms contained in the latter."

In view of the facts embraced under this law, and the close analogy between the act involved in the formation of the double halides and that of the oxygen salts.

I further the similarity between the products so formed, so offers the following explanation for these compounds:

"Two halogen atoms can play the same part that the so-called linking oxygen atom plays in oxygen salts."

This view has been held by some chemists, in more or less modified form, for some time,

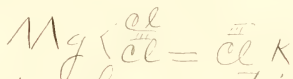




Maquet "in 1867 was the first  
to offer this explanation.  
He explained the compound of Silver  
Chloride and Potassium Chloride as  
the formula



In which the Chlorine is bivalent,  
Blancström (2) in 1869  
offered a somewhat similar  
formula for the double Chloride  
of Magnesium and Potassium,  
thus:-



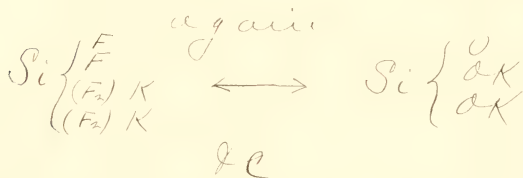
The Chlorine here acting as a trivalent  
element.

(1) "Principes de Chimie fondée sur les Théories Modernes,

(2) "Die Chemie der Jetztzeit vom Standpunkte der electro-  
chemischen Auffassung aus Bezugs- und Lehre entwickelt.



If the view be accepted that the halogen atoms can play the same part as the linking oxygen atoms in a molecule, a close analogy is seen to exist between the oxygen salts and the double halides, thus

$$\text{Al} \begin{cases} (\text{Cl}_2) \text{Na} \\ (\text{Cl}_2) \text{Na} \\ (\text{Cl}_2) \text{Na} \end{cases} \longleftrightarrow \text{Al} \begin{cases} \text{ONa} \\ \text{ONa} \\ \text{ONa} \end{cases}$$


The principal objection urged against this view is that emphasized by Professor Harstemeier (1) namely, that the halogen atoms must be considered to act asivalent elements. But this

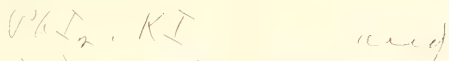


objection can not long stand in  
view of the existence of such com-  
pounds as  $\text{ICl}_3$ ,  $\text{IF}_3$  &c. and  
further the halogens have been  
shown to be polyvalent towards  
oxygen. Therefore it is difficult  
to see why this objection should  
be urged any longer.

By reading the article in  
Graham-Otto's "Lehrbuch der  
Anorganischen Chemie" on the  
combinations of Lead Iodide with  
Potassium Iodide, we cannot  
fail to be impressed with the fact  
that the different combinations of  
these bodies form a well marked  
exception to the law, <sup>mentioned above,</sup> of combination  
of alkali halides with other halides.  
~~mentioned~~ For in addition to



The salts



there are mentioned also the salts



In view of these facts this investigation was undertaken to determine whether the combinations of Lead Iodide with Potassium Iodide really formed an exception to the above law. In order to do this all the work previously done on this subject was carefully repeated & the conditions of the several experiments varied in every way possible.

The investigation was then extended





to the corresponding classes the  
 Braconine Coccipands, with regard  
 to which very little was known.

It was hoped that the work could  
 be extended to the Mueseine Coccipands  
 and to mixed Coccipands containing  
 more than one form, but

this could not be accomplished  
 on account of lack of time.

It is hoped that in the future  
 this portion of the investigation  
 can be completed.

---



## Method of Analysis

It is very peculiar that in giving the results of their work on the double iodides of Lead and Potassium, neither Beathelot nor Stille give the methods used by them for the analysis of the salts, although results are given by each for complete Analyses.

It is difficult to decide just what conclusion to draw from this fact.

To say the least of it they look at it in the most favorable light one would be led to suppose that the analyses of the salts must be such a simple matter that it does not deserve to be



mentioned. However, this is far from the case as after cooking all the subject for two years it will be impossible to absolutely determine the method for complete analysis has yet been found.

The composition of most of the sals prepared in this investigation was deduced from the determination of water of crystallization and Lead.

The water was determined by heating to  $110^{\circ}$  a weighed quantity of the salt dried by pressing carefully between drying paper.

In another portion the Lead was determined thus:—  
a weighed portion of the salt <sup>about 1 gramme</sup> was



introduced into an Erlenmeyer flask of 125 c.c. capacity, Enough concentrated Sulphuric Acid ~~was~~ to decompose the salt was then poured over it. The flask was then inclined to prevent loss by sputtering and a very gentle heat ~~was~~ applied, until all the iodine had been given off, the Lead and Potassium being now in the form of Sulphates.

A close examination of the flask was made that some yellow particles of Lead Sulphide remained undecomposed on the sides of the flask. This was then washed down with concentrated Sulphuric acid, and the mass was now thoroughly boiled for about





amount larger in order to remove  
 the remaining ~~of~~ ~~lead~~ ~~sulphate~~  
 into Sulphate. After cooling  
 the mass was diluted to about  
 100 cc. & a small quantity  
 of Alcohol added to prevent  
 any Lead Sulphate being dissolved.  
 Allowed to stand then until the  
 supernatant liquid was  
 perfectly clear. Then  
 filtered into a Gooch crucible,  
 the ~~filter~~ was then washed  
 thoroughly first with ~~water~~ to  
 which a little sulphuric acid  
 and Alcohol had been added  
 in order to remove all traces  
 of Potassium Sulphate, then  
 washed with water containing a  
 little Alcohol in order to remove



all Sulphuric Acid. The crucible  
was then dried thoroughly at  
 $110^{\circ}$  & finally heated to a very  
low red heat. Then allowed  
to cool twenty minutes in a  
desiccator and weighed.

To determine the Potassium  
by simple evaporation of the  
filtrate containing Potassium  
Sulphate & Sulphuric Acid is  
not at all practicable as  
evaporation of the large excess  
of Sulphuric Acid necessarily  
prevents.

Experiments were made on the  
separation of Lead as Sulphide  
as hydrogen Sulphide, but it was  
found that in every case some of  
the Lead sulphide remained in







in order to insure complete decomposition of the salt, and filtered into a Gooch crucible, without washing, for if water be added to the filtrate Lead Iodide separates.

The Iodine in the filtrate was then precipitated as  $PbI_2$ .

The residue with Gooch crucible was then washed with cold water and the washings again passed through the crucible in order to retain any Lead Iodide which may have separated and to insure all Potassium Iodide being removed from the crucible.

This second filtrate is now added to the first in which there is already





an excess of Silver Nitrate,  
The Silver Iodide was then dried and  
weighed. The Lead Iodide

on the crucible was then dried  
& weighed. As from the combined  
residue of Lead Iodide & Silver  
Iodide the total amount of  
Iodine was calculated,

4: The filtrate from the Silver  
Iodide was then treated with Hydrogen  
Sulphide, in order to remove  
all Lead & Silver, <sup>filtered</sup> and evaporated  
to dryness with Sulphuric acid.

The residue of Potassium Sulphate  
was heated to redness and weighed,  
from which the amount of  
Potassium was calculated.

was used in it, was the same as  
salt obtained by dissolving



Lead Iodide in a hot solution  
of Potassium Iodide, (saturated  
at  $22^{\circ}$ ), and allowing to cool  
gave the following results;  
1. Determination of Water of crystallization.

Weight of salt used = 1.2456 grams

" " water lost 0.0683 "

Percentage of water = 5.47%

2. Determination of Lead.

Weight of salt used = 0.5166 grams,

Lead sulphate formed = 0.3687 "

~~Soluble~~ " " Lead present = 0.2518 "

Percentage of Lead = 30.84%

3. Determination of Silver.

Weight of salt used = 1.4549 grams,

Lead Iodide = 0.9057 "

Silver Iodide = 0.5492 "

Silver Iodide = 0.6220 "

Silver in Silver Iodide = 0.530.



Total weight of Iodine = 0.8350 gms

Percentage of Iodine = 57.37%

Determination of Potassium.

Weight of salt used = 1.4544 gms.

Potassium Sulphate = 0.2018 "

Potassium = 0.0906

Percentage of Potassium = 6.23%

Summary

|           | Found      | Calculated |
|-----------|------------|------------|
| Water     | = 57.47% - | 57.43%     |
| Lead      | = 30.84% - | 31.23%     |
| Iodine    | = 57.37% - | 57.43%     |
| Potassium | = 6.23% -  | 5.91%      |
| Total     | 99.93% -   | 100.00%    |

This composition corresponds calculated  
for the salt  $\frac{1}{2} \text{PbI}_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$   
as it should more exactly  
be written  $\text{K Pb I}_3 \cdot 2\text{H}_2\text{O}$ ,  
the difference being 10.00%



method for determining water of crystallization of Lead was carried out. Therefore, the water was identified by its composition obtained from the determinations of water and Lead. In all the calculations the atomic weights given by Meyer & Schubert were used.

The amount of Lead present in a given amount of Lead sulphate was determined in all the analyses by multiplying the weight of Lead Sulphate by the factor 0.683

---





# Potassium Iodo-Plumbite.

Salt of the Composition,



The first attempt to synthesize of the combinations of Lead Iodide with Potassium Iodide was done by Boullay who, in 1827, announced as the result of his work, the existence of the two salts  $\text{PbI}_2 \cdot \text{KI}$  and  $\text{PbI}_2 \cdot 4\text{KI}$ .

The last named salt forms ~~xxxx~~ a very marked exception to the law of combination of the alkali halides with other halides.

As the work of Boullay had been carried out quite a long time ago, it was to some considerable extent



for at that time quantitative determinations were not so accurate as they might have been, and furthermore the filter pump had not then been invented, so that the methods for preparation of the salts must have been rather crude.

The first efforts were of course directed to the preparation of the salt  $\text{PbI}_2 \cdot \text{KI}$  described by Baillay. The Potassium Iodide used in these experiments was purified by removing any Iodide present by Zinc amalgam. <sup>(1)</sup> The Lead Iodide first used was prepared by precipitating Lead Nitrate solution

<sup>(1)</sup> Moore & Barton, Amer. Chem. Jour. 10-321



with Potassium Iodide. Towards  
the latter portion of the investigation  
Commercial Lead Iodide prepared  
by A. L. Thomsen and Co. of Baltimore  
was used and gave results  
agreeing very well with those  
obtained by using the Lead Iodide  
specially prepared.

According to Baessler, when  
Lead Nitrate is added to a slightly  
concentrated solution of  
Potassium Iodide there is formed  
first a <sup>red</sup> precipitate of Lead Iodide,  
which soon turns white owing  
to the conversion of the Lead  
Iodide into the double salt,  
 $PbI_2 \cdot KI$  by the Potassium  
Iodide present in the solution.  
Great trouble was experienced



at first in preparing this salt,  
as Boullay directed to use a  
solution of Potassium Iodide  
only slightly concentrated,

In each of the preliminary experiments  
Lead Iodide was precipitated when  
Lead Nitrate solution was added  
to a solution of Potassium  
Iodide only slightly concentrated,

But on standing, whether  
cold or hot, there was no  
change to a white color as  
described by Boullay; the  
Lead Iodide remaining unchanged  
in the solution. But when  
a solution of Potassium Iodide  
a little more concentrated was  
used and heat applied it was  
noticed that yellow needles formed





along the upper portion of the beaker in which the experiment was being conducted, where drops of the solution had splattered. These drops becoming more concentrated by evaporation,

This suggested that if a more concentrated solution of Potassium Iodide were used, the salt might be obtained. Experiments were then made to determine the exact conditions under which the salt is formed.

To this effect, a solution of Lead Nitrate was made up so that 1 cc. = 0.25 grammes. To this a Potassium Iodide solution of such a strength that 1 cc. = 0.25 grammes. Five portions of the Lead Nitrate



Solution of fine cubic centimeters each  
measured out,

To these were added quantities  
of Potassium Iodide solution  
(warmed) varying from 5 c.c. to  
25 c.c. Lead Iodide was

precipitated in each case  
but on boiling the mass did  
not turn white as described  
by Baillay, in any of the  
fine portions.

So to fine portions measured (5 c.c. each)  
of the Potassium Iodide solution  
were added successively quantities  
of ~~the~~ solid Potassium Iodide  
varying from 0.25 gm. to 1.25 gm.  
Three solutions were heated &  
added to the fine portions  
of the Lead Nitrate solution,



Lead Iodide was ~~formed~~ precipi-  
-tated in each case but still there  
was no double salt formed.  
So again to five portions (5 c.c. each)  
of the <sup>potassium iodide solution</sup> ~~red~~ solution of  
Potassium Iodide, varying from  
3.0 gms to 5.0 gms. The solutions  
were then heated and added to  
five portions (5 c.c. each) of the Lead  
Nitrate solution. Lead Iodide  
was precipitated in each case  
but gradually the red precipitate  
became white, the next portion  
being solution becoming white with  
on heating these masses the  
white salt is decomposed  
and insoluble Lead Iodide remains  
having the form of the original  
crystals but ~~not~~ on cooling the



... white, using  
 to the maximum of the sample  
 such as described by Baillay.  
 This slightly yellowed salt was  
 freed from the mother liquor  
 as much as possible by means  
 of a filter pump. Then pressed  
 between drying paper & then  
 placed in a desiccator for two  
 hours. The following results  
 were obtained by analysis:

1. Determination of water of crystallization

weight of salt used = 0.7777 gms

water lost = 0.0111 "

percentage of water = 1.14 %

2. Determination of Lead

weight of salt used = 1.6154 gms

Lead Sulphate = 0.7023 "

Lead = 0.1111 "





Percentage of Lead - 29.70%

3. Determination of water of crystallization  
 after standing over sulphuric acid over night  
 weight of salt used = 1.0204 gms.

" " water lost = 0.0028

Percentage of water = 0.27%

### Summary

|         |               |         |        |                                 |
|---------|---------------|---------|--------|---------------------------------|
|         | 1%            | Fanning | -      | Calculating for                 |
|         |               | 2%      |        | PH <sub>2</sub> S, KI (Bauchop) |
| Water - | 1.14%         | -       | 0.273% |                                 |
| Lead -  | <b>29.70%</b> |         |        | 33.02%                          |

Clearly this salt lost its water of crystallization by standing over sulphuric acid, a dehydrating agent. One therefore should not be prepared in this way to see a white solid as it is. The crystals after standing have long needles of slightly yellowish tint. By a slight



elevation of temperature these needles  
are redissolved in the mother  
liquor, but by rapidly heating  
the beaker containing the mass with  
a ~~small flame~~ ~~small flame~~ ~~small flame~~  
decomposed. Lead dioxide remain-  
ing, which retains the form of  
the original crystals. Recasting  
these needles again, becomes white,

The explanation of the formation  
of these long-needles in the  
mother-liquor will be given  
under the head of the salt,  
3  $\text{PbI}_2$ , 4  $\text{KI}$ , 6  $\text{H}_2\text{O}$ .

The salt  $\text{PbI}_2$ ,  $\text{KI}$  (Bailey)  
was then prepared in larger  
quantities by using the  
saccharine of ~~potassium~~,  
4 grams. Lead Nitrate were dissolved in



15 c.c. of water. So 15 grams of KI were dissolved in 15 c.c. of water, the solution was then filtered and added to the Lead Nitrate solution, cooled rapidly, stirring all the while, the double salt thus formed was pumped dry & pressed between drying paper for twenty four hours.

This salt gave on analysis the following results,

1) Water in terms of water of crystallization

a) weight of salt used = 3.0712 gms

" " water lost = 0.0712 "

Percentage of water = 5.22%

b) weight of salt used = 1.1614 gms

" " water lost = 0.0610 "

Percentage of water = 5.25%



## 2% Determination of Lead

a) weight of salt used = 1.0744 "

Lead Sulfate = 0.4842 "

" " Lead = 0.3307 "

Percentage of Lead = 30.78 %

b) weight of salt used = 1.3640 gms.

" " Lead Sulfate = 0.6162 "

" " Lead = 0.4209 "

Percentage of Lead = 30.86 %

c) weight of salt used = 0.8867 gms.

" " Lead Sulfate = 0.4002 "

" " Lead = 0.2733 "

Percentage of Lead = 30.82 %

## Summary

Found

Calculated for  
 $\text{PbI}_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$

1% + 2% - 3% —

Water - 0.22 + 0.20 — 5.43

Lead - 30.78 + 30.86 + 30.82 + 31.23

From these figures the composition





if the salt is deduced as

$KPhI_3 \cdot 2H_2O$  or  $PhI_2 \cdot KI \cdot 2H_2O$ .

Baillouy prepared this salt in solid if not Liq., according to the former only 3% of water & says "Si l'on suppose pur, l'iodure sel, les deux iodures soient à l'état d'hydriodates, il faudrait 4.16 d'eau pour 100 parties du sel humide; or on n'en trouve que 3." "In speaking of the formation of this salt Baillouy states that it is always formed when a slightly concentrated solution of Potassium Iodide is brought together. Lat or coel with an

(D. Ann. Chim. Phys [2] - 34 - 367)



excess of Lead Iodide. It is  
 apparent in our tests why  
 we should have made this  
 statement as it is evident from  
 his work on the subject that  
 he never worked with an  
 excess of Lead Iodide, but  
 that in each case Lead Iodide was  
 first precipitated & this was then  
 converted into the double salt  
 as Iodo-plumbite by the excess  
 of KI in the solution.

However, in order to test his  
 statement strictly ~~according~~  
~~to his own words~~, a solution  
 of Potassium Iodide not  
 quite saturated at  $20^{\circ}$  was  
 added to a large excess of Lead  
 Potassium Iodide in a beaker



was stirred thoroughly. On first  
cooling the excess of Lead Iodide  
precipitated at the bottom while the  
superficial liquid remained  
clear. But on the following  
day silky, needle shaped crystals  
were found in the solution &  
also mixed with <sup>pure</sup> Lead Iodide  
in the bottom. The crystals  
were removed from the solution  
dried and analysed giving the  
following results,

Determination of Lead

Weight of salt used = 0.2150 gms

Lead Sulphate = 0.0957

" " Lead = 0.0654

Percentage of Lead = 30.42%

Theoretical for  $K_2PtI_6 \cdot 2H_2O$  = 31.23%

This is therefore the same salt as



3

Some of the needle shaped crystals  
of the salt  $KPH_2$ , 2 H<sub>2</sub>O were then  
heated to 140° to test whether any  
water could be driven  
off but a greater loss was  
found than by heating to 100°.  
So there are only two molecules  
of water of crystallization bound  
in the salt.

The further apart the bones upon  
the saet was tried in this way,  
some of the wood & shap. sticks  
were placed in the ignition like  
this in turn was placed in the  
~~xx~~ ~~sticks~~ ~~sticks~~ ~~sticks~~ ~~sticks~~ ~~sticks~~  
That the temperature raised  
gradually, at 70° water began  
to be given off, the saet becoming





a brighter yellow, but decomposing  
considerably in bulk, as the  
temperature rose & as the amount  
of water given off increased to  
such an extent that it collected  
in large drops on the side  
of the tube. These drops,  
falling on the sac, began  
decomposed it instantly as  
was shown by the color of  
the dead inside which  
appeared. Thus the same  
water which had been present  
in the Campanula as water  
of crystallization after having  
been once driven out by heat  
served to decompose the acetylene  
sac when brought in contact  
with it. By using an



27  
ignition tube bent at an angle  
in order to prevent the water  
falling back upon the salt  
it was shown that at about  
 $310^{\circ}$  the salt decomposed, iodine  
being given off.

Treated with muscic acid  
this salt is decomposed just  
as when treated with water.

---







This formula was based upon  
the following analyses,

|                  | <u>Found</u>                   |                                | <u>Calculated for</u>           |
|------------------|--------------------------------|--------------------------------|---------------------------------|
|                  | <u>1<sup>st</sup> analysis</u> | <u>2<sup>nd</sup> analysis</u> | <u><math>PbI_2 + 4KI</math></u> |
| Lead Iodide      | 34.0                           | 36.0                           | 41.0 %                          |
| Potassium Iodide | 66.0                           | 64.0                           | 59.0 %                          |

Efforts were made to  
to repeating this work, in  
order to see whether the salt  
really existed; for if it  
exists it forms a very  
striking exception to the  
law of combination of the  
alkali halides with other  
halides mentioned in  
the introduction.

In a lead saturated solution  
of Potassium Iodide, Lead  
Nitrate was added & a yellowish





white salt was obtained.

This was the first crop of Lead & Potassium Iodides obtained in this investigation, and was dried neat by pumping off the mother liquor but for simple filtration, then pressed between drying paper for a short while & finally <sup>completely</sup> dried by standing over Lime, the method adopted by Baillay.

This salt gave on analysis the following results,



### 1. Determinations of water of crystallization

a) weight of salt used = 1.2961 gms.

" " water lost = 0.0388

Percentage of water = 2.99%

b) weight of salt used = 1.2734 gms.

" " water lost = 0.0191

Percentage of water = 1.50%

### 2. Determinations of Lead

a) weight, salt used = 0.3880 gms.

of Lead Sulphate = 0.00351

" " Lead = 0.0980

Percentage of Lead = 25.26%

b) weight salt used = 2.3640 gms.

of Lead Sulphate = 0.9015

" " Lead = 0.6007

Percentage of Lead = 26.04%

Calculated

Found

Calculated for  
PbO, 25.26%

water of crystallization

2.99 1.50

Lead 25.26 26.04 18.40%



These results show that plainly  
the salt  $\text{PbI}_2 + 4\text{KI}$  had not  
been obtained but rather a  
salt approaching in  
composition the salt  
 $\text{PbI}_2, 2\text{KI}, 4\text{H}_2\text{O}$  with ~~the~~ described  
by Ritté<sup>(1)</sup> & ~~also described~~  
with the exception of the water, which  
is shown by the difference in the  
two analyses, <sup>the</sup> second having <sup>been</sup> made  
several days after the first, but  
water was abstracted by the  
sieve over which the salt stood.

The preparation of this salt &  
its analyses were rather  
crude as they were the first  
attempts; however ~~the~~ ~~of~~ ~~was~~  
the results were sufficient to



show that the salt  $\text{PbI}_2 \cdot 4\text{KI}$  had not been pressed under the conditions named.

Later in the investigation another attempt was made to prepare this salt following the directions of Baucay, but the salt instead of being dried over Lime was pressed for several days between drying paper & carefully analysed.

The following results were obtained,

1<sup>st</sup> Determinations of water of crystallization

a) weight of salt used = 1.2106 gms.

" " water lost = 0.0634 "

Percentage of water = 5.24%





b) - weight of salt used = 0.9371 gm  
water lost = 0.1000

Percentage of water = 5.23%

### 2% Determinations of Lead

a) weight of salt used = 0.9371 gm

" " Lead Sulphate = 0.4567

" " Lead = 0.3121 "

Percentage of Lead = 30.95%

b) - weight of salt used = 0.8693 gm.

" " Lead Sulphate = 0.3914 "

" " Lead = 0.2673 "

Percentage of Lead = 30.75%

Summary

Found

1% Analysis, 2% Analysis

Calculated  
for  $\text{PbI}_2 \cdot 4\text{KI}$

Water = 5.23

Lead { 30.95 { 30.75 { 18.40

Theoretical Composition of  $\text{PbI}_2 \cdot 4\text{KI} \cdot 2\text{H}_2\text{O}$

gives Water = 5.43, Lead = 31.23



The salt therefore is plainly the  
salt  ~~$\text{PbI}_2 \cdot \text{H}_2\text{O}$~~ .  ~~$\text{PbI}_2 \cdot 2\text{H}_2\text{O}$~~   
 $\text{K PbI}_3 \cdot 2\text{H}_2\text{O}$ .

Two results differed very widely  
from those first obtained in  
trying to prepare the salt

$\text{PbI}_2 \cdot \text{H}_2\text{O}$ . The first was  
the ~~first~~ percentage of Lead was  
25.26% in the second case  
30.95%. Many efforts

were then made to obtain  
the salt which yielded 25.26%  
of Lead. Varying the con-  
ditions in all possible  
ways, but in no case was  
anything obtained even

approaching this composition,  
therefore it seems probable  
is concluded that the salt was



25.26% which was prepared & analysed in a rather rough way must have been nearly impure owing to excess of Potassium Iodide present.

From the above facts it is to be concluded that the salt  $\text{PhI}_2 \cdot 4\text{KI}$  does not exist, & that it probably consisted of the salt

$\text{KPhI}_3 \cdot 2\text{H}_2\text{O}$  mixed with quite a large amount of Potassium Iodide.



III. Salt of the Composition, K<sub>5</sub>PG I<sub>7</sub> (PGI, 5KI). -

W. I. W. H.

The salt of this composition is mentioned in Graham-Atta's "Lehrbuch der Anorganischen Chemie" and is ascribed to Baullay, but no reference is given to the article in which Baullay describes this salt.

All the articles of Baullay on this subject were then carefully examined, but no such salt could be found. On searching through the Jahrbuchricht of Berzelius & the Jahrbuchricht now published, no account of this salt could be found. But in order to make the proof of its non-existence





still more positive all the  
journals in the Chemical  
Library of the Johns Hopkins  
University were examined.

This work consumed about  
~~two~~ months time and as a

result no trace of the salt  
 $\text{PhI}_2 \cdot 5\text{KI}$  could be found.

Further, in all the experiments  
on the combinations of Iodine  
Iodide with Potassium Iodide

there was at no time found a  
salt whose composition

approached in any degree the  
formula  $\text{PhI}_2 \cdot 5\text{KI}$ .

Therefore it is <sup>most</sup> probable that

this is an error in the "Lehrbuch  
der Anorganischen Chemie".

---



IV. Salts of the Composition,  $K_2PtI_4 \cdot 11H_2O$  ( $PtI_2 \cdot 2KI \cdot 4H_2O$ )<sup>37</sup> and  
 $K_2PtI_4 \cdot 2H_2O$  ( ~~$PtI_2 \cdot 2KI \cdot 3H_2O$~~ ).  
~~These salts are described in the paper by Berthelot.~~  
~~They are described in the paper by Berthelot.~~  
~~They are described in the paper by Berthelot.~~

Since the paper published by Boulay in 1827, the principal work on the double iodides of Lead & Potassium has been done by Litte & also by Berthelot.

Litte<sup>38</sup> described the salt  $PtI_2 \cdot 2KI \cdot 4H_2O$ , giving an account of its method of formation, appearance, general behavior & studied its decomposition by water.

Berthelot<sup>39</sup> has taken up the subject and described the two

(1) Ann. Ch. Phys. [5] - 24 - 226

(2) Ann. Ch. Phys. [5] - 29 - 289



salts  $\text{PbI}_2$ ,  $2\text{KI}$ ,  $2\text{H}_2\text{O}$  acid  
 $3\text{PbI}_2$ ,  $4\text{KI}$ ,  $6\text{H}_2\text{O}$ .

The investigation was then  
turned back to the repetition  
of the work of these chemists  
and agree that the salts  
 $\{\text{PbI}_2, 2\text{KI}\} \cdot 4\text{H}_2\text{O}$  and  $\{\text{PbI}_2, 2\text{KI}\} \cdot 2\text{H}_2\text{O}$   
are formed

and agree that the salt containing  
Lead & Potassium Iodides in the  
proportion of one part of Lead Iodide  
to two of Potassium Iodide is  
formed whenever Lead Iodide  
is added to a warm solution  
of Potassium Iodide & the solution  
allowed to cool. Little also  
states that the salt is formed  
in the cold.

As previously stated when this



crystallization was first begun a salt was obtained which seemed to have the composition  $\text{Ph}_2\text{I}_2\text{N}_2$ .

The water of crystallization not being constant.

But when in the first attempt to repeat the work of Nitte, a salt was obtained, resembling in appearance that described by Nitte but which an analysis gave the following results—

1. determination of water of crystallization

weight of salt used = 1.2227 gms.

water lost = 0.0413 "

Percentage of water = 3.38%





2. Determination of Lead

a) - weight of salt used: 2.221 gms

Lead Sulphate = 0.9541

" " Lead 0.6517 "

Percentage of Lead = 30.23 %

b) - weight of salt used = 0.9733 gms

Lead Sulphate = 2.1

" Lead 0.2934

Percentage of Lead = 30.14 %

### Summary

|        | <u>1st analysis</u> | <u>2nd analysis</u> | <u>Calculated for</u><br><u><math>PbI_2 \cdot 2KI \cdot 4H_2O</math></u><br><u>5.43 %</u> |
|--------|---------------------|---------------------|-------------------------------------------------------------------------------------------|
| Lead - | 30.28               | 30.14               | 23.93 %                                                                                   |

This composition agrees more closely with the salt  $KI_2 \cdot 2KI \cdot 4H_2O$  for which the water = 5.43 % & Lead = 21.23 % The water of crystallization varies here because the salt was finally dried and hence,



The salt just mentioned has been  
 known from a hot solution,  
 as it has been known earlier  
 that heat decomposes the salt  
 $PbI_2, KI, 2H_2O$ . When iodide separating  
 from the mass, it was thought  
 probable that the salt  $PbI_2, 2KI, 4H_2O$   
 would be formed in the cold.

To this end, 15 c.c. of a cold saturated  
 solution of Potassium Iodide was  
 added to 10 c.c. of a cold saturated  
 solution of Lead Nitrate.

The Lead Iodide precipitated soon  
 turned white owing to the forma-  
 tion of the double salt,

as the mass became pasty more of  
 the Potassium Iodide solution was  
 added, enough to render the  
 mass quite ~~fluid~~ <sup>mobile</sup> & to increase



all Lead Iodide being converted into the double salt.

The salt prepared in this case was analysed by boiling with Sodium Carbonate, the Lead being thus changed to Carbonate, which is a more easily soluble. soaked thoroughly & ignited on a low red heat. The Lead was then weighed as Lead Oxide. The following results were obtained,

15. Determinations of water of crystallization

a) weight of salt used = 1.7823 gms.

" " water lost = 0.0966 "

Percentage of water = 5.42 %

b) weight of salt used = 1.6530 gms.

" " water lost = 0.0892

Percentage of water = 5.39 %



## 2. Re-amination of Lead.

weight of salt used = 1.7823 gms.

" Lead iodide = 0.5990 "

Lead = 0.5560

Percentage of Lead = 31.20%

### Summary.

|  | Found        | Calculated for |
|--|--------------|----------------|
|  | 2 quantities | KTg. 2 1/2 0   |

|       |         |         |           |
|-------|---------|---------|-----------|
| Water | { 5.42  | { 5.39  | { 5.43 %  |
| Lead  | { 31.20 | { 31.23 | { 31.23 % |

is this method, after preparing the salt <sup>(indicated)</sup> 2 1/2 0, has failed, it was then attempted to prepare the salt by heating a cold saturated solution of Potassium Iodide almost to boiling then adding Lead Iodide to saturation, but this was found impracticable since such large quantities of Lead Iodide are taken





up by the solution that the double  
salt begins to separate from the  
solution at the surface while  
Lead Iodide is still being  
taken up.

So to a hot solution  
of Potassium Iodide (cold saturated)  
Lead Iodide was added in quite  
large quantity but not enough  
to cause the separation of  
the salt as mentioned above.

An amazing pale-yellow, needle  
shaped crystals separated.  
These were dried & <sup>weighed</sup> ~~labelled~~ #1.

The filtrate from this salt was  
moderately diluted with water  
& soon the light colored crystals  
were seen to appear. On standing  
a short while, the whole mass became  
almost solid, owing to the thick



network of needles shaped crystals  
formed. These were dried &  
marked #2. By continuing the  
dilution crystals began to appear  
again but upon adding more  
water these crystals were transformed  
into Lead Iodide & Potassium Iodide  
however on stirring the mass  
thoroughly the original white  
color was restored. These  
crystals were dried & marked #3.  
By further dilution of the filtrate  
still a faint crop of crystals  
was obtained. These were marked  
#4. But upon adding ~~more~~  
water to a small portion of the filtrate  
a copious crop of Lead Iodide  
separating in  
large quantities.

~~(2) By further dilution a similar crop of crystals  
was obtained which were marked #5.~~



But authentic needles portion of the  
 fictitious with Alcohol, a flocculent,  
 white sact separated which on  
 close examination seemed to be  
 composed of little needles.  
 These were marked #5.

It was thought that these fine specimens  
 would prove to be a series of  
 compounds showing a variation  
 in composition.

The following results were obtained  
 from the analyses.

Determinations of water of crystallization

#1) - weight of sact. used = 1.5388<sup>gms</sup>  
 water lost = 0.0813

Percentage of water = 5.28%

#2) - weight of sact. used = 1.2032<sup>gms</sup>  
 water lost = 0.0617 "

Percentage of water = 5.13%



#3) weight of sact used = 1.2780 gms

" " water lost = 0.0673 "

Percentage of Water = 5.27%

#4) weight of sact used = 1.1226 gms

" " water lost = 0.0590

Percentage of water = 5.26%

#5) - weight of sact used = 1.2413 gms

" " water lost = 0.0631

Percentage of water = 5.15%

2% - determinations of Lead

#1) weight of sact used = 1.6216 gms

" Lead Sulphate = 0.7300 "

" " Lead = 0.4986 "

Percentage of Lead = 30.75%

#2) weight of sact used = 1.1767 gms

" " Lead Sulphate = 0.5391 "

" " Lead = 0.3612

Percentage of Lead = 30.76%





#3) - weight of salt used - 1.2780 gms.

Lead Sulfate - 0.3912

" " Lead = 0.3749

Percentage of Lead = 30.90%

#4) - weight of salt used = 1.1226 gms

Lead Sulfate - 0.5016

" " Lead = 0.3481

Percentage of Lead = 31.01%

#5) weight of salt used = 1.2413 gms

" " Lead Sulfate = 0.5637 "

" " Lead = 0.3850

Percentage of Lead = 31.02%

### Summary

#1 #2 <sup>4</sup>gms #3 #4 #5 calculated for  
K<sub>2</sub>PbF<sub>6</sub> · 2H<sub>2</sub>O

Water { 5.28 { 5.13 { 5.27 { 5.26 { 5.15 } 5.43 %

Lead { 30.75 { 30.76 { 30.90 { 31.01 { 31.02 } 31.23 %

The results are known in almost all of the analyses below the theoretical. This is to be expected as the material is pure which



is used in Potassium Iodide cannot be washed out but has to be processed out. This caused therefore some results in water & lead to fall below the theoretical.

An examination of the above table shows that instead of obtaining a series of salts, the same salt has been obtained in each case, becoming gradually poorer as the solution was diluted.

Bailey observed this same phenomenon.

These facts also show that the same salt  $KPhI_3 \cdot 2H_2O$  is obtained & not Mitche's salt  $PhI_2 \cdot 2KI \cdot 4H_2O$  whether a hot concentrated solution of Potassium Iodide be used or a cold solution decreasing from considerable



concentration to just above the point where separation of Lead Iodide takes place. It will further illustrate separation the same salt from this last most dilute solution.

This is very strong evidence against the existence of the salt  $PbI_2 \cdot 2KI \cdot 4H_2O$  described by Little or  $PbI_2 \cdot 2KI \cdot 2H_2O$  described by Rothstein.

Another solution was then prepared similar to that from which the salt marked #1 had been obtained but, instead of pouring from the crystals formed, water was added. Lead Iodide at first separated but by stirring the mass thoroughly the original color was restored. In this way



a large quantity of water was added until finally by further addition of water to a small portion of the mass the iodide was seen to separate & remain so on stirring thoroughly.

The analysis of the salt thus formed proved it to be the salt  $KPtI_3 \cdot 2H_2O$ .

Efforts were then made to prepare the salt  $PtI_2 \cdot 2H_2O$  by dissolving the salt  $KPtI_3 \cdot 2H_2O$  ( $PtI_2 \cdot KI \cdot 2H_2O$ ) in a large excess

of a cold saturated solution of Potassium Iodide. Heat being applied the salt dissolved and on cooling long needle shaped crystals separated similar in appearance to the salt which had been dissolved. The following result was obtained by analysis





# determination of Lead

weight of sac used = 1.0974 gms

" " Lead Sulphate = 0.4742

" " Lead = 0.3375 "

Percentage of Lead = 30.75%

Theoretical for  $\text{KPHI}_3 \cdot 2\text{H}_2\text{O}$  = 31.23%

All of these attempts to prepare ~~the~~ <sup>the</sup> sac described in each letter & Berthelot having failed, it was concluded to try once again, following the directions of "Mitte" exactly. In this way

a sac was prepared which when heated, before <sup>being</sup> separated from its mother liquor, decomposed, the Lead Iodide so formed retaining the form of the original crystals, in picturing water and allowing

van. Ch. Phys [5] : : : :



to cool a wet mass of needle shaped crystals was obtained which almost solidified the mass,  
 An analysis of this salt gave the following results,

1. Determination of water of crystallization  
 weight of salt used = 1.2172 gms  
 " water lost = .1650 "

Percentage of water = 5.34 %

2. Determination of Lead.

weight of salt used = 0.8487 gms

" " Lead Sulphate = 0.3836 "

" " Lead = 0.2620 "

Percentage of Lead = 30.87 %

Summary

Found : } for  $PbI_2 \cdot KI \cdot 2H_2O$  } for  $PbI_2 \cdot 2KI \cdot 4H_2O$   
 Calculated

|       |           |         |         |
|-------|-----------|---------|---------|
| Water | { 5.34 %  | 5.23 %  | 5.33 %  |
| Lead  | { 30.87 % | 31.23 % | 43.93 % |

This was therefore the same as the



as has been obtained in all the  
 previous experiments.

Witte<sup>11</sup> describes another method  
 for the preparation of the salt  
 $\text{PbI}_2, 2\text{KI}, 4\text{H}_2\text{O}$ ; so as all  
 previous efforts to prepare the  
 salt had failed it was thought  
 this might by this means the  
 salt might be obtained as  
 in the other cases very conclusive  
 evidence obtained that the  
 salt does - exist.

This method of preparation consists  
 in mixing freshly precipitated  
 Lead Carbonate with an excess  
 of a cold saturated solution of  
 Potassium Iodide. No action  
 takes place if and in any experiment.

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but on passing a current of carbon dioxide through the mixture for about twenty minutes, the white Lead Carbonate is replaced by the slightly yellowish crystals of the double salt. This salt, on analysis the following results,

1. Determination of water of crystallization  
weight of salt used = 0.9316 gms.

" " water lost = 0.0492.

Percentage of water = 5.28%

2. determinations of Lead

a) - weight of salt used = 1.0653 gms

Lead Sulphate = 0.4908 "

" " " = 0.3372 "

Percentage of Lead = 31.47%

b) - weight of salt used = 0.8595 gms

" " Lead Sulphate = 0.3958 "

" " Lead = 0.2703 "

Percentage of Lead = 31.47%





# Summary

Found

1.28 - 2.5

Calculated for  
 $K_2 PbI_2 \cdot 2 H_2O$ 

|       |       |       |       |
|-------|-------|-------|-------|
| Water | 1.28  | 31.45 | 31.23 |
| Lead  | 31.47 | 31.45 | 31.23 |

The salt  $PbI_2 \cdot 2KI \cdot 2H_2O$  described by Bercholat<sup>11</sup> was obtained, to use his own words "par le froidissement de la solution de l'iodure de plomb dans une solution concentrée d'iodure de potassium".

Mainly this condition has been tried repeatedly in the effort to prepare the salt  $PbI_2 \cdot 2KI \cdot 4H_2O$  described by Little, but in order to be absolutely certain that this ~~is not~~ salt of Bercholat's

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not be prepared, three successive attempts were made varying the conditions slightly in each case. The salts obtained in this way gave an analysis the following results,

~~1) Determination of water of crystallization~~

#1) - weight of salt used = 1.0975 gms

" " water lost = 0.0565 "

Percentage of water = 5.15%

#2) - weight of salt used = 1.3876 gms

" " water lost = 0.0724 "

Percentage of water = 5.22%

#3) - weight of salt used = 0.9158 gms

" " water lost = 0.0477 "

Percentage of water = 5.21%



## 2. Determinations of Lead.

#1)- weight of salt used = 1.3778 gms

" " Lead Sulphate = 0.6141 "

" " Lead = 0.4194 "

Percentage of Lead = 30.44%

#2)- weight of salt used = 0.6197 gms.

" " Lead Sulphate = 0.2738 "

" " Lead = 0.1870 "

Percentage of Lead = 30.34%

#3)- weight of salt used = 0.8046 gms

Lead Sulphate = 0.3569 "

" " Lead = 0.2438 "

Percentage of Lead = 30.30%

## Summary

| 1%    | 2%   | 3%    | Calculated for          |                      |
|-------|------|-------|-------------------------|----------------------|
|       |      |       | $K_2PtCl_6 \cdot 2H_2O$ | $PbCl_2 \cdot 2H_2O$ |
| 1.1   | 2.2  | 3.3   | 3.3                     | 4.4                  |
| 30.11 | 30.1 | 30.30 | 30.3                    | 30.3                 |

Showing that all of the three salts do  
have the composition  $K_2PtCl_6 \cdot 2H_2O$ .



Solutions of Potassium Iodide saturated at  $100^{\circ}$  were then worked with  $\text{KCN}$ , <sup>was</sup> some failed to keep no value as when ~~only~~ a ~~small~~ rather small quantity of Lead Iodide was added, then on cooling a large mass of Potassium Iodide crystallized out along with the double salt, and when a large quantity of  $\text{PbCN}_2$  was added the mass soon became unmanageable on account of the large amt of double salt present in the solution, so that it could not be filtered or purified in any way.

From all of the above facts it is to be concluded that the salts





$KPH_2$ ,  $2H_2O$  ...  $KPH_2$ ,  $2H_2O$  ...  
can not exist; for not only  
have the directions of both  
Nette & Bendelat been closely  
followed but in view of the  
furthermore the conditions  
have been changed, using at  
one time hot solutions at  
another cold, at one time  
cold saturated at another  
dilute, again a solution  
of  $KI$  saturated it was  
employed, in each case the  
salt  $KPH_2$ ,  $2H_2O$  was obtained,  
further it was attempted to make the  
salt by dissolving  $KPH_2$ ,  $2H_2O$  in  
a cold saturated solution of Potassium  
Iodide & finally by passing Carbon Dioxide  
through a mixture of Lead Carbonate







(4) slow cooling of the mother liquor from the salt  $\text{Pb}_{1/2} 2\text{K}_{1/2} 2\text{H}_2\text{O}$  which in turn is prepared by adding Lead Iodide to a concentrated solution of Potassium Iodide.

These fractions were closely followed. The mother liquor from the salt which first separated on cooling being surrounded by water in order to lower the temperature & was then allowed to stand four days.

Long <sup>yellow</sup> needles separated which an analysis showed the potassium iodide -

12 - Determination of water of crystallization.

weight of salt used = 0.7837 gms.

" " water lost = 0.0382

Percentage of water = 4.87%



## 2. Determination of Lead

weight of salt used = 0.9913 gms

" Lead Sulphate = 1.002 "

" " Lead = 0.2740

Percentage of Lead = 27.64%

## Summary

|       | Found | Calculated for                                                                                    |
|-------|-------|---------------------------------------------------------------------------------------------------|
|       |       | $3\text{PbI}_2, 4\text{KI}, 6\text{H}_2\text{O} = 2\text{PbI}_2, 3\text{KI}, 4\text{H}_2\text{O}$ |
| Water | 4.87  | 5.02 %                                                                                            |
| Lead  | 27.64 | 27.75 %                                                                                           |

This analysis seemed to show that the salt has the composition  $2\text{PbI}_2, 3\text{KI}, 4\text{H}_2\text{O}$ .

In order to confirm this the experiment was repeated, the mother liquor in this case being surrounded by ice. Long needles crystallized from the solution, but in addition considerable quantities of





Potassium Iodide also separated,  
 so the whole was heated gently  
 until all had passed into  
 solution. The beaker was then  
 placed on a block in the Laboratory  
 and allowed to cool.

The following night was very  
 cold and on examining the  
 beaker next morning there  
 could be seen half the crinkle  
 sack of Potassium Iodide.  
 This was heated until well dissolved,  
 & after several trials at different  
 temperatures finally a good  
 crop of beautiful long needles  
 was obtained which were  
 apparently free from Potassium  
 Iodide. This fact is very  
 significant regarding results.



1<sup>st</sup> Determination of water of Crystallization  
weight of salt used = 1.2129 gms  
" water lost = 0.0647

Percentage of water = 5.33 %

2<sup>nd</sup> Determination of Lead,

weight of salt used = 0.6945

" Lead Sulphate = 0.3140

" " Lead = 0.2145

Percentage of Lead = 30.88 %

Summary

Found

Calculated for  
 $K_2PbI_4 \cdot 2H_2O$

Water { 5.33 } 5.43 %

Lead { 30.88 } 31.23 %

These results showed that  
most probably in the first  
preparation of the salt,  
the temperature was reduced  
too low so that the salt was



mixed with Potassium Iodide,  
In order to test this view & to  
confirm the last experiment  
the work was very carefully  
repeated. Accurate measure-  
ments being made at each  
stage, as follows:-  
100 cc. of a solution of KI <sup>(cont. at 22°)</sup> was  
heated <sup>in a water bath</sup> & when the  
temperature <sup>inside</sup> reached 75° was added gradually  
while the temperature was being  
raised to 100°. In this way  
17.5084 <sup>gms. of Potassium Iodide</sup> were added,  
The solution was then allowed  
to cool. At 34° needle shaped  
crystals began to separate.  
The cooling was continued  
until the temperature reached  
22°, the mother liquor was



then pumped off & replaced under  
 a ~~vacuum~~ jar bell jar when it was  
 allowed to remain for three  
 days, the temperature varying  
 only slightly above or below  
 $18^{\circ}$ . Long needle shaped  
 crystals separated as before  
 and apparently pure for use  
 Potassium Iodide.

An analysis of this salt gave  
 the following results:-

Determination of water of crystallization  
 weight of salt used = 1.263 gms  
 water lost = 0.0474 "

Percentage of water = 3.75%

Determination of Lead

weight of salt used = 1.2400 gms

" " Lead Sulfate = 0.5548 "

Lead = 0.3789

Percentage of Lead = 30.56%





## Summary

|       | <u>Found</u> | <u><math>KPhI_3 \cdot 2H_2O</math></u> | <u>Calculated for</u><br><u><math>3PhI_2 \cdot 4KI \cdot 6H_2O</math></u> |
|-------|--------------|----------------------------------------|---------------------------------------------------------------------------|
| Water | 51.12        | 51.43%                                 | 51.02%                                                                    |
| Lead  | 30.96        | 31.23%                                 | 28.82%                                                                    |

From these facts it seems probable that the salt described by Berthelot as  $3PhI_2 \cdot 4KI \cdot 6H_2O$  was really a mixture of the salts  $KPhI_3 \cdot 2H_2O$  and  $KI$ .

Indeed this is rendered quite probable when it is remembered that at the temperature & concentration used, Potassium Iodide which is present in the solution in large excess, separates very easily as already shown.



Sodium Iodide Reversible in

the literature in regard to this subject is extremely limited.

Bancroft<sup>(1)</sup> states that it is behavior like other alkali ~~halides~~ <sup>halides</sup> in regard to ~~the~~ <sup>the</sup> formation of the double halide, but makes no experiments on the subject.

Witte<sup>(2)</sup> discusses the subject by stating that Sodium Iodide behaves like Potassium Iodide but gives no experimental data.

Paggiani<sup>(3)</sup> mentions a double iodide of Lead & Sodium to which he assigns the composition  $Pb_2NaI$ , but this work

1. Jour. Chem. Phys. 21 21 312

2. Comp. Rend. 72 155

(3) Jour. fur Prakt. Chem. 35 329



is not all reliable,

Efforts were made to obtain this salt so that it could be analyzed & its composition determined. To this effect, 700 grms. of Sodium Iodide were dissolved in 750 cc. water at 20°. Lead Iodide was then added until no more dissolved. About 60 grms. being thus added.

This solution on standing gave back to no crystals. The <sup>heavier</sup> salt in solution is therefore much more soluble than the corresponding potassium salt.

The solution was then heated & 10 grms. more of Lead Iodide added. On cooling nothing crystallized out.

The solution was then evaporated to about  $\frac{2}{3}$  of its former size.



in solution with stop. crystals  
 separated closely resembling the  
 Potassium salt, in appearance,  
 these crystals formed in such  
 large quantities that the mass  
 almost completely solidified,  
 Like the Potassium salt, this  
 salt is decomposed by water  
 & by heat with a separation of  
 Lead Iodide. Great difficulty  
 was experienced in purifying  
 this salt, for such large quantities  
 of Sodium Iodide were mixed  
 with it. Various methods were  
 tried, for example, as Sodium  
 Iodide is very deliquescent it was  
 hoped that by allowing the mixture  
 to stand exposed to moist air enough  
 water would be taken up to dissolve





The Sodium Iodide I leave the double  
sack behind but this proved  
unavailable, the method finally  
adapted was as follows:-

The mixture was exposed to the  
air until quite a considerable  
quantity of water had been ~~absorbed~~,  
The undissolved portion ~~was~~ being  
pressed with a slapping rod was  
a gritty feel due to the Sodium  
Iodide present. It was then  
gently applied & it was soon  
found that the gritty feel had  
disappeared, only a few sacks  
remaining in the solution,  
The heating was now discontinued  
& the mass filtered rapidly by means  
of a filter pump. (For if the heating  
is continued the whole passes into solution.)



The salt was then packed between  
drying paper for several days &  
at the end of that time was found  
to be still moist & showing  
that the salt itself was deliquescent.  
It was then dried in an air bath at

100°C. The anhydrous salt,  
which is a reddish-yellow  
granular solid is the following  
results:-

### Determination of Lead

Weight of salt used = 0.8511 gms.

Lead Sulfate = 0.4326

Lead = 0.2407

Percentage of Lead = 34.71%

Theoretical for  $\text{NaPhI}_3$  = 33.89%

The composition of the salt is  
therefore very probably  $\text{NaPhI}_3$ ,  
Nothing definite can be said in



regard to the water of crystallization  
as the salt is so deliquescent that  
it cannot be obtained dry at  
ordinary temperatures,  
However it is very probable that  
the salt does contain water of  
crystallization we account  
~~for its~~ <sup>for its</sup> tendency to the ~~stagnation~~  
salt & from the fact that so much  
Sodium iodide crystallizes out  
with the double salt, the solution  
becoming very concentrated,  
probably on account of so  
much water being taken up by  
the ~~double~~ <sup>double</sup> Sodium iodides to  
form water of crystallization  
in the double salt.

---



Pressure Points Analysis

The only work ~~done~~ on this subject up to the present time was that done by Berthelot<sup>11</sup>. This was very unsatisfactory however & indeed he remarks that the substances obtained by him are not to be regarded as true chemical compounds, but as mixtures of the double salt with Potassium Bromide or Lead Bromide. He gives however the composition of the salt obtained as



Efforts have been made to determine whether a definite compound

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if Lead by Potassium Bromide, which  
 he obtained. It was found  
 that if to a solution of Potassium  
 Bromide saturated at  $20^{\circ}$ , a solution  
 of Lead Nitrate (saturated at  $20^{\circ}$ ) be  
 added, drop by drop, the Lead Bromide  
 so formed will be dissolved on  
 constant stirring until quite  
 a large quantity has been  
 dissolved. Though not nearly so  
 large a quantity as in the case  
 of the Iodides. It was found that  
 Lead Bromide possibly had been  
 dissolved the solution was allowed  
 to stand and in about three hours  
 colorless crystals began to form,  
 after several days these <sup>tabular</sup> crystals  
 grew to considerable size. ~~They~~  
 On analysis the following results were obtained,  
 from the finely powdered salt,



Determinations of water of crystallization

a) weight of salt used = 0.7823 gms

" " water lost = 0.0236

Percentage of water = 3.53%

b) weight of salt used = 1.1592 gms

" " water lost = 0.0381

Percentage of water = 3.31%

2% - Determinations of Lead

a) weight of salt used = 2.051 gms

" " Lead Sulphate = 0.7497 "

" " Lead = 0.5120 "

Percentage of Lead = 40.80%

b) weight of salt used = 2.281 gms

" " Lead Sulphate = 0.5570 "

" " Lead = 0.3804

Percentage of Lead = 40.92%

Summary

|       | Found<br>in analysis 2% analyzed |       | Calculated for<br>K <sub>2</sub> PbO <sub>4</sub> · 2H <sub>2</sub> O |
|-------|----------------------------------|-------|-----------------------------------------------------------------------|
| Water | 3.53                             | 3.49  | 3.57%                                                                 |
| Lead  | 40.80                            | 40.92 | 41.06%                                                                |



This salt was prepared repeatedly  
afterwards & its analyses leave  
no doubt but that the composition  
is  $KPhBr_3 \cdot H_2O$ . The crystal  
form in every case was  
the same.

Similar

Efforts were made to prepare  
the corresponding Sodium  
Bromo Plumbite, but all failed.  
It was thought at one time that  
the salt had been obtained as  
needle shaped crystals separated  
from the solution of Lead  
Bromide in Sodium Bromide.  
But this proved on analysis  
to be Lead Bromide.

Efforts were also made to prepare  
this salt by using hot Sodium Bromide









in investigation was then turned  
to the preparation of this salt,  
Potassium Chloro-Plumbite,

A cold saturated solution of  
Potassium Chloride was heated  
to boiling & a solution of Lead  
Nitrate (cold saturated) added  
gradually, the mass being  
continuously stirred, & see below  
on cooling a salt crystallized  
out in fine white needles which  
on analysis showed the  
following results,

1. Analysis of Lead.

|                          |        |       |
|--------------------------|--------|-------|
| wt weight of salt used = | 1.2142 | grams |
| " " Lead Sulphate =      | 1.0281 | "     |
| " " Lead =               | 0.7022 | "     |
| Percentage of Lead =     | 57.84  | %     |

x Lead chloride was dissolved but not so  
much as the Lead salt as in the case of the Lead Nitrate.



Wt. weight of salt used = 1.2039 gms

Lead Sulphate = 1.0176

Lead = 0.6950

Percentage of Lead = 57.73

Summary

Found  
1<sup>st</sup> analysis    2<sup>nd</sup> analysis

Calculated for  
K<sub>2</sub>PbCl<sub>3</sub>

Lead { 57.81 } 57.73 { 58.71

There is no water of crystallization in this salt.

Instead of cooling the solution rapidly as was done above, if it be cooled slowly & kept at about 35° the Potassium Chloro Plumbite can be obtained in lustrous crystals somewhat needle shaped, these crystals have the same composition as the above analysed salt but the solution is more



mechanically held in the crystal, for  
on heating to about  $200^{\circ}$  the salt  
precipitates just as Potassium  
Chloride does when heated.  
These salts are necessarily  
impure inasmuch as  
the large excess of Potassium  
Chloride present in the solution  
remains.

All attempts to prepare Lithium  
Chloro-Plumbite failed.

A salt crystallizing in rectangular  
leaflets was obtained but this in  
analysis was proved to be  
Lead Chloride.

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The work on the Fluor-Plumbites  
could not be carried to any extent  
on account of the want of time,  
but a few qualitative experiments  
showed that a cold saturated  
solution of ~~Lead~~ <sup>Potassium</sup> Nitrate ~~xxx~~ he  
added to a cold saturated solution  
of Potassium Fluoride heated  
almost to boiling, a small  
portion of the Lead Fluoride  
so formed is dissolved,  
But less of the Lead salt is  
dissolved in this case than  
in ~~xxx~~ the case of either the  
Iodide, Bromide, or Chloride,

It was hoped that his investigation  
could be extended to the mixed halides,  
but want of time prevented this.





## Conclusions —

The principal results of this investigation may be summed up as follows,  
1<sup>st</sup> — Of the six Iodo Plumbites of Potassium described by Saucy, Klotz, & Berthelot, only one exists, that is the Salt  $K Pb I_3 \cdot 2 H_2 O$

2<sup>nd</sup> The Bromo Plumbite of Potassium is a well crystallized compound having the composition  $K Pb Br_3 \cdot H_2 O$

3<sup>rd</sup> — The Chloro Plumbite of Potassium can also be prepared in well formed crystals & has the composition  $K Pb Cl_3$ .



4% The quantity of the Lead Halide dissolved in the alkaline halide increases with the atomic weight of the Halogen, thus only a small quantity of Lead Fluoride dissolves in <sup>Calcium</sup> Potassium Fluoride, a larger quantity of Lead Chloride in Potassium Chloride solution, a still larger quantity of ~~Potassium~~ Lead Bromide in Potassium Bromide & greatest of all Lead Iodide in Potassium Iodide solution.

5% That the corresponding Sodium salts are, if forced, separated with great difficulty as in the case of the Soda Plumbite, while no such case

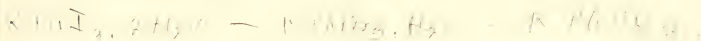


isolated in the case of the Sodium  
Bromo or chloro Plumbite,

6% That all of these salts are  
decomposed by water, & in  
order for these salts to exist  
in solution a certain mini-  
-mum amount of alkali  
halide must be present.

This amount varying inversely  
as the atomic weight of the  
halogen atom present in the  
Compound.

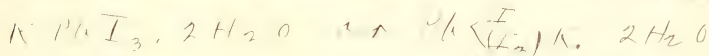
7% That the water of crystallization  
decreases as the atomic weight  
of the halogen decreases, thus,





8<sup>o</sup> Finally it is seen that the composition of all these salts allows them to be expressed by formulas in which two halogen atoms play the part of a linking oxygen atom, thus proving these salts to be no exception to the law of combination of alkali halides with other halides first formulated by Professor Remyer & mentioned in the introduction to this investigation.

These salts are to be represented thus,







A possible explanation of the results obtained by Baillay, Mitte & Benichat is this:- In preparing the Soda Plumbites, two salts are used, Lead Iodide and Potassium Iodide, neither of which contains any water of crystallization. Now the Soda-plumbite of Potassium contains two molecules of water of crystallization, if the solutions are concentrated then in the formation of the Soda-plumbite a large amount of this water is taken up as water of crystallization, by the Soda-plumbite. This would serve to concentrate the solution very much & would thus cause a



12  
separation of potassium iodide  
which is present in large  
quantities excess.

This caused cause the analyses  
of the salts to show a much  
larger proportion of Potassium  
Iodide than ~~actually~~ belongs  
to the true compound.

Place other exceptions to the  
law of combination in the  
double halides have been found  
viz,  $\text{Pu Cl}_2 \cdot 4 \text{KCl} \cdot 3 \text{H}_2\text{O}$  described  
by Poggendorff;  $\text{Th Cl}_3 \cdot 2 \text{KCl}$   
described by Wadsworth and  
 $\text{Ce Cl}_3 \cdot 2 \text{KCl}$ , described by Wadsworth.  
In regard to the salts of the  
Mn, G. M. Richardson working  
in this Laboratory has shown



conclusively that this salt does not exist, and similarly, Mr. C. E. Saunders also working in this Laboratory, has shown that the salt  $5KCl_3 \cdot 6CoCl$  does not exist.

Finally in regard to the salt  $CoCl_2 \cdot 2KCl$  the evidence points at present to the correctness of this formula, but more work is still needed on this compound.

This last salt therefore is the only real exception to the law as put forward by Professor Riesen.

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Biographical

The author of this dissertation  
was born at Milledgeville, Ga.,  
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In 1879 he entered the Middle Georgia  
Military and Agricultural College at  
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